Three-dimensional Orientational Photocontrol of Liquid-Crystalline Molecules in Photoresponsive Polymer Networks[1]

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Three-dimensional orientation of liquid crystal molecules is induced by slantwise non-polarized visible light irradiation of a composite of a nematic liquid crystal and crosslinked polymer networks with azobenzene side chains, exhibiting rewritability and storage stability.

Recently, much attention has been paid to the orientational control of photochromic molecules such as azobenzenes by means of photoinduced alterations of molecular structures as well as orientations of photoactive molecules.[2] For example, when azobenzenes are tethered to an outmost surface of substrate plates of a cell filled with a nematic liquid crystal (LC), the alignment of the LC becomes photocontrollable as a result of the marked amplification of photochemical transformations of command layers.[3] We reported previously the conoscopic observation implying that the orientational direction of a nematic LC is determined specifically by the incident direction of actinic light when the cell is subjected to slantwise irradiation.[4,5] In connection with the working mechanism of this kind of surface-assisted photoalignment, we have revealed that the slantwise photoirradiation of thin films of amorphous[6] as well as liquid-crystalline[7] polymers bearing azobenzene side chains brings about the photo-reorientation of azobenzene chromophores in such a way that the reorientational direction is in accordance with the incident direction of the light. These results have led us to achieve the surface-assisted generation of homogeneous alignment of nematic LCs with pretilt angles.[6,8] On the other hand, we have described an alternative route to perform the photoalignment of LC molecules by employing a hybrid system, comprised of a low-molecular weight LC and a crosslinked polymer network with azobenzene side chains, which is subjected to linearly polarized light irradiation.[9] This kind of network-mediated photocontrol of the azimuthal LC alignment is achieved as a result of the marked amplification of photo-reorientational alteration of a small amount of azobenzene residues studded to polymer networks. We report here that the irradiation with non-polarized light of the LC / azobenzene polymer composite is a promising technique to achieve the three-dimensional control of the orientation of LC molecules filled in volume-type cells.

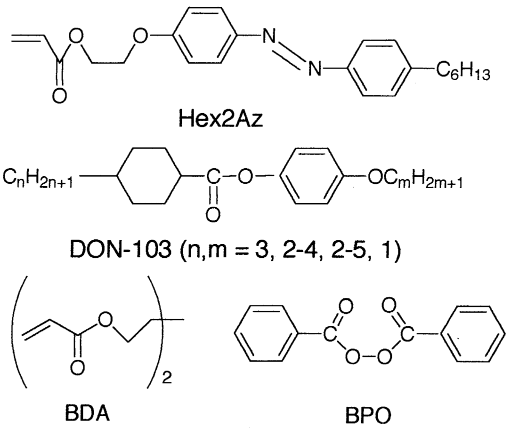

Figure 1. Chemical structures of compounds used in this study.

Chemical structures of materials used here are shown in Figure 1. A cell filled with LC / photoactive polymer network was fabricated according to our previous paper.[9] A homogeneous solution of benzoyl peroxide (BPO), 4-hexyl-4'-(2-acryloxyethoxy)azobenzene (Hex2Az) and a nematic LC, DON-103 (T_{NI} = 73 °C), in dichloromethane was evaporated *in vacuo* at room temperature, followed by mixing with 1,4-butanediol diacrylate (BDA). The mixture consisting of 5 wt% of BPO, 5 wt% of Hex2Az, 30 wt% of BDA and 60 wt% of DON-103 was sandwiched between two glass plates and sealed. The cell gap was adjusted to be 25 μm by using film spacers. Conoscopic observation at room temperature revealed that the mixture is in an isotropic phase. The cell was heated at 80 °C for 10 min to achieve the radical polymerization. Consequently, slight light scattering was observed at room temperature because of phase separation. A clearing point was checked by orthoscopic observation and determined to be 47.5 °C as a transition temperature between nematic and isotropic phases (T_{NI}), which was much lower than that of pure DON-103, reflecting the presence with various components.

The polymerized cell was exposed to non-polarized 436 nm light at 50 °C slightly higher than the T_{NI} of the polymerized mixture. Irradiation conditions expressed by azimuthal (α) and polar (β) angles of light are illustrated in Figure 2. Conoscopic observation of the cell at room temperature revealed the appearance of a crosspoint as shown in Figure 2 (a), indicating the generation of homeotropic alignment, when the cell was subjected to the photoirradiation with light-1 from the surface normal (α = 0° and β = 0°). A minimum exposure dose required for the emergence of the clear crosspoint was about 500 mJ cm^{-2}. When the light incidence was switched to slantwise irradiation expressed as light-2 (α = 180° and β = 45°), the crosspoint was shifted to the left side (Figure 2 (b)). The direction of the shift coincided with the incident direction of light-2, which came from the left side of the conoscopic images. After the attainment of the photostationary position of the crosspoint, the cell was exposed subsequently to light-3 (α = 0° and β = 45°) as illustrated in Figure 2. The crosspoint moved to the right side through the homeotropic position (Figure 2 (c)). At the photostationary state, the tilted direction of optical axis was consistent with the propagation direction of light-3. It should be mentioned here that the photoalignment induced by non-polarized visible light is temperature dependent. No clear crosspoint of a conoscopic image was observed even after irradiation with light-1 at an exposure dose of 15 J cm^{-2} at room temperature. Similar

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phenomenon was reported in the case of linearly polarized light irradiation of this type of a volume-type LC cell.[9] The heating at temperatures above the T_{NI} of the mixture enhances the molecular mobility of the hybrid system. The generation of optical anisotropy under the conditions, where the LC is in anisotropic phase, stems probably from the maintenance of ordered structures of LC molecules in microscopic domains incorporating the azobenzene residues.

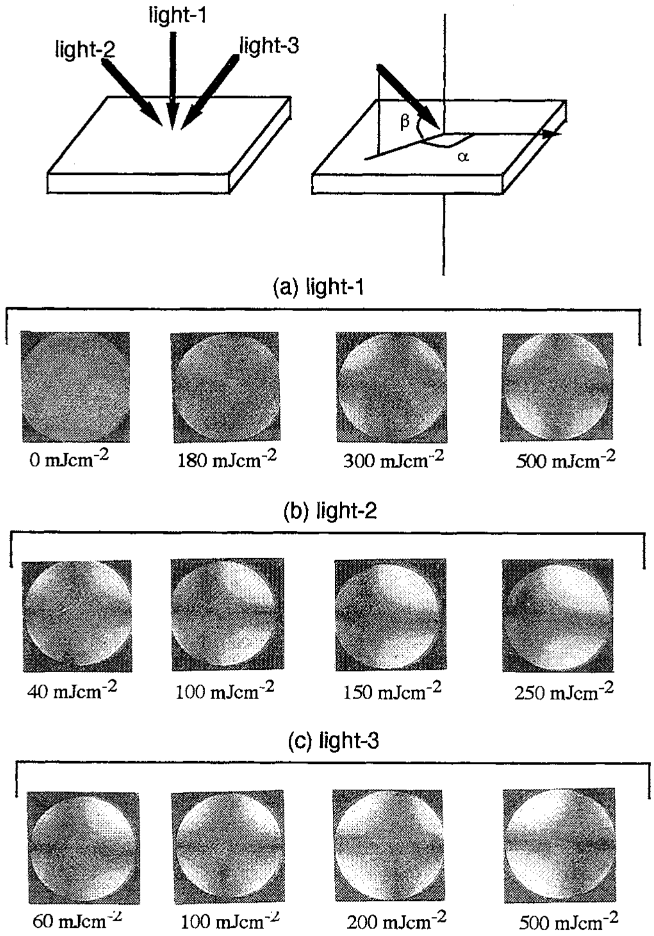

Figure 2. Conoscopic observation of a polymerized cell during slantwise exposure to 436 nm light. The incident direction of the light and exposed light energy are indicated in the figure.

The present observation can be interpreted as follows. Irradiation with 436 nm light induces the repetition of E/Z photoisomerization of the azobenzene moieties to result in the molecular reorientation in such a way that the π,π^* transition moment of the azobenzene molecules lies in parallel with the propagation direction of the light to minimize the light absorption.[6] The reorientation of the azobenzene side chains triggers the modification of anisotropic alignment of LC molecules surrounding them. Both of the crosslinked polymer network and the cooperative work of LC molecules suppress efficiently the molecular motion of photo-reoriented azobenzenes, which act as command molecules to give uniform alignment of a bulk LC phase upon cooling down.

In summary, the prominent photocontrol of three-dimensional orientation of LC molecules in a volume-type cell filled with an LC / crosslinked polymer composite has been realized by slantwise irradiation with non-polarized light. This type of the LC composite system is rewritable by exposure to non-polarized light under various irradiation conditions determined by both of azimuthal and polar directions and accordingly applicable to novel photonics elements and devices.

References and Notes

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